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New smelting process for titanium: Magnesiothermic reduction of  $\text{TiCl}_4$  into liquid Bi  
and subsequent refining by vacuum distillation

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## Abstract

We demonstrate a new continuous smelting process for Ti that combines magnesiothermic reduction of  $\text{TiCl}_4$  into liquid Bi and refining by vacuum distillation.  $\text{TiCl}_4$  is reduced by Mg into liquid Bi to form Bi–Ti liquid alloys, and subsequently refined by vacuum distillation. The Bi–Ti liquid alloys can be easily transferred from a reduction vessel to a refining vessel; consequently, the reduction and refining steps can be performed continuously. Bi–Ti alloys with various compositions were confirmed to form, and the compositions were controllable via adjustment of the nominal composition of  $\text{TiCl}_4$ , Mg, and Bi. After reduction, the alloys were efficiently separated from  $\text{MgCl}_2$  by differences in their densities. In addition, vacuum distillation of the alloys purified Ti to be greater than 99.6 at%. Moreover, consideration of the heat balance in the reduction step indicated that the proposed process has the potential to unlimitedly improve the feed rate of  $\text{TiCl}_4$  when the concentration of Ti in the alloy is 6–7 at%.

Keywords: continuous smelting process of Ti, Bi-Ti liquid alloy, heat balance

## 1. Introduction

Recently, we reported the electrochemical reduction of  $\text{TiO}_2$  into a liquid Bi cathode to produce Bi–Ti liquid alloys in molten  $\text{CaCl}_2$  [1]. This process has the potential to improve the productivity of Ti because the reduction and refining steps can be performed continuously using the liquid alloys. However, in this process, Ca co-deposition into liquid Bi easily occurs during the reduction step because of the very low activity coefficient of Ca in Bi, which inhibits the formation of the Bi–Ti alloy. In contrast, electrolysis of  $\text{TiCl}_2$  in  $\text{CaCl}_2$  produces Bi–Ti alloys with a relatively high concentration of Ti and little Ca contamination. Thermodynamic considerations based on potential- $\text{pO}^{2-}$  ( $= -\log a_{\text{O}^{2-}}$ ) diagrams indicate that it is important to maintain a high  $\text{pO}^{2-}$ , *i.e.*, a low concentration of  $\text{O}^{2-}$  in the melt. However, a high  $\text{pO}^{2-}$  near the  $\text{TiO}_2$  cathode is difficult to achieve because  $\text{O}^{2-}$  ions are formed at the  $\text{TiO}_2$  cathode during reduction.

In the present study, we propose an alternative process involving Bi–Ti liquid alloys; this process is based on the Kroll process used in current industry. The remarkable advantage of this process is a cooling effect of liquid Bi during the reduction step of the Kroll process, which leads to an increased Ti production rate. Similar processes involving Ti–Zn liquid alloys have been examined by Gleave *et al.* and Sato

*et al.* [2,3]. According to the Ti–Zn phase diagram [4], the solubility of Ti in Zn at 900°C (13 mol%) may be sufficiently large for this phase to function as a liquid alloy. Although high vapor pressure of Zn ( $9.5 \times 10^{-1}$  atm at 900°C [5]) is advantageous for vacuum distillation, we believe that the high vapor pressure is an obstacle during reduction to realize a practical process. In comparison to Zn, Bi has a lower vapor pressure of  $1.9 \times 10^{-3}$  atm and a larger solubility of Ti (*i.e.*, 30 at% at 900°C) [5,6]. Sb is also a potential solvent for Ti because its vapor pressure and solubility of Ti are  $2.3 \times 10^{-2}$  atm and 16 at% at 900°C, respectively [5,7]. For vacuum distillation, Zn is the superior solvent, followed by Sb and Bi. However, for reduction, Bi is the most appropriate solvent because it has the greatest solubility of Ti and the lowest melting point (272°C) among Bi, Sb, and Zn. A low melting point is an important property for a material to function as a cooling agent and is a key to improving the feed rate of  $\text{TiCl}_4$  with removing the large amount of heat generated in the reduction step. In this study, we propose an alternative continuous smelting process for the mass production of Ti and experimentally investigate the magnesiothermic reduction of  $\text{TiCl}_4$  into liquid Bi and subsequent refining of Ti by vacuum distillation.

## 2. Smelting process for Ti using Bi–Ti alloys

Figure 1 shows the schematic illustration of the proposed new process.  $\text{TiCl}_4$  is reduced by Mg into liquid Bi to form Bi–Ti alloys according to the following reaction.



Given the solubility of Ti in Bi and the vapor pressure of Bi, the temperature of the reduction cell should be 900°C [5,6]. Refining by vacuum distillation is subsequently performed after the alloys are tapped out to the refining vessel from the bottom of the reduction vessel. Vacuum distillation of the alloys is performed at temperatures higher than 1000°C, and the recovered Bi can be reused for the reduction step. Molten  $\text{MgCl}_2$ , which is byproduct of the reduction step, is also tapped out, and electrolysis is conducted to recover Mg metal and  $\text{Cl}_2$  gas. The outstanding feature of this process is the cooling effect of Bi. Bi removes heat caused by magnesiothermic reduction of  $\text{TiCl}_4$ , which is a highly exothermic reaction; therefore, the feed rate of  $\text{TiCl}_4$  can be dramatically improved. In addition, the alloys are liquid at operating temperature, which enables a continuous process of reduction and refining. Moreover, the whole process is very similar to the Kroll process, except for the use of liquid Bi, hence, a part of the equipment used in the Kroll process can be utilized in the proposed process. The purpose of this study is to demonstrate the feasibility of the proposed new process using Bi–Ti liquid alloy and verify that the cooling effect of Bi can enhance the feed rate of

TiCl<sub>4</sub>.

### 3. Experimental

#### *Magnesiothermic reduction of TiCl<sub>4</sub> into liquid Bi*

Figure 2 shows the experimental apparatus for the magnesiothermic reduction of TiCl<sub>4</sub> into liquid Bi. Mg (99.9%, Wako Pure Chemical Industries, Ltd.) and Bi (99.999%, Kamioka Mining & Smelting Co., Ltd.) were mixed in several compositions. The mixtures were heated to 750 or 900°C in a MgO crucible under an Ar atmosphere, and then TiCl<sub>4</sub> (> 99.0%, Wako Pure Chemical Industries, Ltd.) was introduced at a rate of approximately 10 g h<sup>-1</sup> using a peristaltic pump. After a certain amount of TiCl<sub>4</sub> was introduced, the temperature was maintained for 1 h at 750, 900, or 1000°C. The reaction temperature ( $T_1$ ), holding temperature ( $T_2$ ), and nominal compositions are summarized in Table 1. The obtained alloys were cooled in the furnace, and were identified by energy-dispersive X-ray spectroscopy (EDAX VE-9800) using a scanning electron microscope (KEYENCE VE-7800).

#### *Vacuum distillation*

First, to prepare homogeneous Bi–Ti alloy, a mixture of Bi and Ti (> 99.0%,

Wako Pure Chemical Industries, Ltd.) with a ratio of 65:35 at% was annealed at 1000°C in a closed cell and was subsequently quenched in water. The prepared Bi–Ti alloy was then placed in a MgO crucible, as shown in Fig. 3, and subjected to vacuum distillation at 1000°C for 24 h. Then, the furnace was cooled to room temperature, and the obtained Ti was evaluated by EDX.

#### 4. Results and discussion

##### *Magnesiothermic reduction of $TiCl_4$ into liquid Bi*

Table 1 presents the EDX results, and the Ti yields which was estimated from the Ti contents of the alloys determined by EDX and the theoretical Ti amounts calculated from nominal compositions of the starting materials assuming that the reaction proceeded completely. In some conditions, the alloy was not completely separated from  $MgCl_2$ . Hence, the alloy accumulated at the bottom of the crucible was examined by EDX, and the Ti yield was determined considering reaction efficiency as well as separation process. In addition, because the Ti distribution is not homogeneous, EDX was performed for several cross-sectional areas of the alloys, and the average compositions were summarized in Table 1. The Ti contents in the alloys were determined to be 7.9–33.4 at% Ti. The composition of the alloy was controlled via adjustment of the nominal composition. Figure 4 shows the Ti yield plotted as a



function of the ratio of the Ti concentration in the alloy to the Ti solubility in Bi at various holding temperatures. The legend denotes the holding temperatures and Ti solubility at each temperature. A lower ratio corresponded to a higher yield of Ti. This result is attributed to formation of the homogeneous liquid alloy without solid compounds. A Ti concentration over the Ti solubility in Bi forms solid compounds with high concentrations of Ti (*e.g.*,  $\text{Bi}_9\text{Ti}_8$ , see Fig. 6), and these compounds adhere to and remain on the wall of the crucible. The reason why the Ti yield is over 100% in Exp. #5 is that the Ti-rich part was analyzed by EDX due to the inhomogeneous distribution. Thus, it is important to prepare homogeneous liquid alloys by maintaining a Ti concentration sufficiently lower than the solubility of Ti. In addition, we investigated how efficiently the alloy can be separated from  $\text{MgCl}_2$ . Figure 5 shows the optical cross-sectional images of the Bi–Ti alloys obtained after Exps. #3, 4, and 6. In the case of Exp. #3, the alloy existed as a mixture with  $\text{MgCl}_2$  and was difficult to separate. One of the possible reasons for this difficulty of separation is that solid  $\text{Bi}_9\text{Ti}_8$ , formed at reaction interfaces, hindered migration of the liquid alloy and molten  $\text{MgCl}_2$ . In fact, a decrease in the Ti content in the alloy improved the separation at the same holding temperature (Fig. 5b, Exp. #4). Similarly, elevation of the holding temperature achieved efficient alloy separation (Fig. 5c, Exp. #6). All separation results are summarized in

Table 1. These results can be explained by the Bi–Ti phase diagram. The alloy in Exp. #1 consists of a liquid phase and solid  $\text{Bi}_9\text{Ti}_8$ . The composition of the alloy in Exp. #3 is almost on the solubility line, but a huge amount of  $\text{Bi}_9\text{Ti}_8$  formation is expected at reaction interfaces in the alloy during the reaction. The state of other alloys is liquid, and the concentration is far from the solubility line. The latter alloys are more easily separated from  $\text{MgCl}_2$  than the former. Thus, efficient alloy separation requires the Ti concentration in the liquid alloy far from the solubility because it is difficult to prepare Ti-concentrated liquid alloys near to saturation. The higher solubility in Bi than that in Zn and Sb has therefore the great advantage.

### ***Vacuum distillation***

After the alloy containing 35 at% Ti was kept in vacuum at 1000°C for 24 h, the obtained Ti was analyzed by EDX. The Ti purity was as high as 99.6 at% (suppose the rest of 0.4 at% is Bi), thereby indicating that vacuum distillation is a viable refining technique. The remaining Bi could be removed via the manufacture of Ti ingots by vacuum arc re-melting or electron-beam melting, etc. Nevertheless, further investigation of the vacuum distillation conditions as well as the apparatus is still needed for realizing an effective continuous process. In addition, whereas the Ti concentration is low in the

alloy obtained in the reduction step as mentioned above, segregation is able to increase the Ti concentration before vacuum distillation according to the Bi–Ti phase diagram.

### ***Heat balance consideration***

The magnesiothermic reduction of  $\text{TiCl}_4$  is a highly exothermic reaction, which results in a slow feed rate of  $\text{TiCl}_4$ , in other words, a low production rate of Ti in the Kroll process. Here, we consider the heat balance to demonstrate that the cooling effect of Bi can enhance the feed rate of  $\text{TiCl}_4$ . The considered scheme is illustrated in Fig. 7. The concept is based on the idea that heat generated by reduction of  $\text{TiCl}_4$  is used to heat Bi for maintaining the temperature of the reduction cell. First, the following conditions are assumed for the reduction process:

1. The temperature of the reduction cell is  $900^\circ\text{C}$ .
2.  $\text{TiCl}_4$  is transferred at  $25^\circ\text{C}$  and is introduced into this reduction cell maintained at  $900^\circ\text{C}$ . The feed rate of  $\text{TiCl}_4$  in the Kroll process is  $n = 4 \text{ L min}^{-1}$  [8,9].
3. Mg is recovered via electrolysis of  $\text{MgCl}_2$  at  $670^\circ\text{C}$  and is introduced into the reduction cell maintained at  $900^\circ\text{C}$ .
4. Liquid Bi recovered by vacuum distillation is transferred at  $300^\circ\text{C}$  and is introduced into the reduction cell maintained at  $900^\circ\text{C}$ .

5. The Bi–Ti alloys are formed at 900°C.
6. Heat dissipation occurs from the reduction cell.

Accordingly, the following six enthalpy changes should be considered for heat balance in this system:

$\Delta H_1$ : Magnesiothermic reduction of  $\text{TiCl}_4$

$\Delta H_2$ : Heating of  $\text{TiCl}_4$  ( $25 \rightarrow 900^\circ\text{C}$ )

$\Delta H_3$ : Heating of Mg ( $670 \rightarrow 900^\circ\text{C}$ )

$\Delta H_4$ : Heating of Bi ( $300 \rightarrow 900^\circ\text{C}$ )

$\Delta H_5$ : Formation of the Bi–Ti alloy

$\Delta H_{\text{diss}}$ : Heat dissipation

$\Delta H_1$  depends on the feed rate of  $\text{TiCl}_4$ ,  $n$ , and  $\Delta H_4$  as well as  $\Delta H_5$  are determined by the composition of the alloy. Here, the heat balance condition to satisfy is described as follows:

$$\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_{\text{diss}} = 0, \quad (2)$$

where  $\Delta H_1$ ,  $\Delta H_2$ ,  $\Delta H_3$ , and  $\Delta H_4$  are taken from available thermodynamic data [5,10,11].

$\Delta H_5$  is the enthalpy of mixing, which is calculated by the following equation according to the regular solution model.

$$\Delta H_5 = \Omega x_{\text{Bi}} x_{\text{Ti}} + \Delta H_{\text{fus}}(\text{Ti}) x_{\text{Ti}} \quad (3)$$

Here,  $\Omega$  is the interaction parameter,  $x_i$  is the mole fraction of  $i$  ( $i = \text{Bi, Ti}$ ) in the alloy, and  $\Delta H_{\text{fus}}(\text{Ti})$  is the fusion enthalpy of Ti. The parameter  $\Omega$  was determined according to the following equation:

$$RT \ln \gamma_{\text{Ti}} = \Omega (1 - x_{\text{Ti}})^2, \quad (4)$$

where  $\gamma_{\text{Ti}}$  is the activity coefficient of Ti in the Bi-Ti liquid alloy, which was determined by emf measurements in NaCl–KCl–TiCl<sub>2</sub> (1 mol%) at 700°C using the Bi–Ti alloy (15 at% Ti) and Ti electrodes (the details of these measurements will be discussed separately).  $\Delta H_{\text{fus}}(\text{Ti})$  is given by the available literature [5].  $\Delta H_{\text{diss}}$  was determined by the heat balance in the Kroll process, as expressed by the following equation.

$$\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_{\text{diss}} = 0 \quad (5)$$

The relationship between  $x_{\text{Ti}}$  and  $n$  was determined from eqs. 2–5, as shown in Fig. 8. The results show that, at  $x_{\text{Ti}} = 0.1$  this process clearly achieves a more than twofold increase in the feed rate of TiCl<sub>4</sub> compared to that in the Kroll process. Assuming  $n = 4$  L min<sup>−1</sup> in the Kroll process, for example, this process exhibits  $n = 9.4$  L min<sup>−1</sup> with  $x_{\text{Ti}} = 0.1$ . Moreover, the results indicate that the feed rate of TiCl<sub>4</sub> can be unlimitedly improved when  $x_{\text{Ti}}$  is controlled to be 0.06–0.07. Thus, our results demonstrate that the cooling effect of Bi results in a significant enhancement of the feed rate of TiCl<sub>4</sub>.

## 5. Conclusions

A new smelting process for Ti using liquid Bi was demonstrated. The composition of the Bi–Ti alloy was optimized to be 6–10 at% to work not only as an appropriate solvent for Ti but also as an effective cooling agent in the reduction step. Such a low concentration allowed efficient separation of the alloy from  $\text{MgCl}_2$ , and resulted in a high yield of Ti in the reduction step. However, further investigation of the vessel materials is necessary to establish this process because MgO crucibles, which were used in this study, increase the oxygen content in Ti to a certain degree. Fe and Mo are prospective materials for the vessel.

### **Acknowledgement**

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## List of table and figure captions

Table 1 Conditions and results of reduction of  $\text{TiCl}_4$ . Ti yield was calculated from nominal compositions and the Ti contents determined by EDX.

Exp.	$T_1 / ^\circ\text{C}^{*1}$	$T_2 / ^\circ\text{C}^{*2}$	Nominal / at%			EDX result / at% <sup>*3</sup>			Ti yield / %	Alloy separation
			Bi	$\text{TiCl}_4$	Mg	Bi	Ti	Mg		
#1	750	750	38.9	22.1	39.0	74.6	22.0	3.4	59	Bad
#2	750	900	55.7	16.5	27.8	81.4	15.3	3.3	63	Good
#3	900	900	31.0	22.4	46.6	64.2	33.4	2.4	72	Bad
#4	900	900	75.8	7.3	16.9	83.0	7.9	9.1	98	Good
#5	900	900	75.4	7.9	16.7	86.9	10.2	2.9	115	Good
#6	900	1000	31.5	21.3	47.2	55.2	28.5	16.3	76	Good

\*1 Reaction temperature, \*2 Holding temperature, \*3 Area analyses (size: 12–27  $\text{mm}^2$ ).



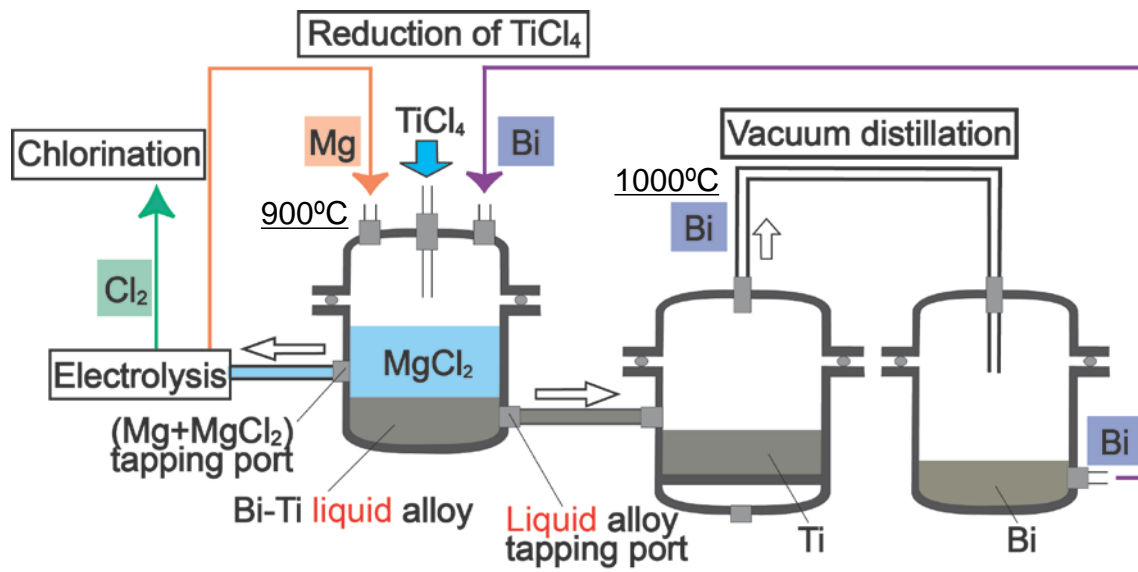


Figure 1 Proposed continuous smelting process for Ti using liquid Bi.

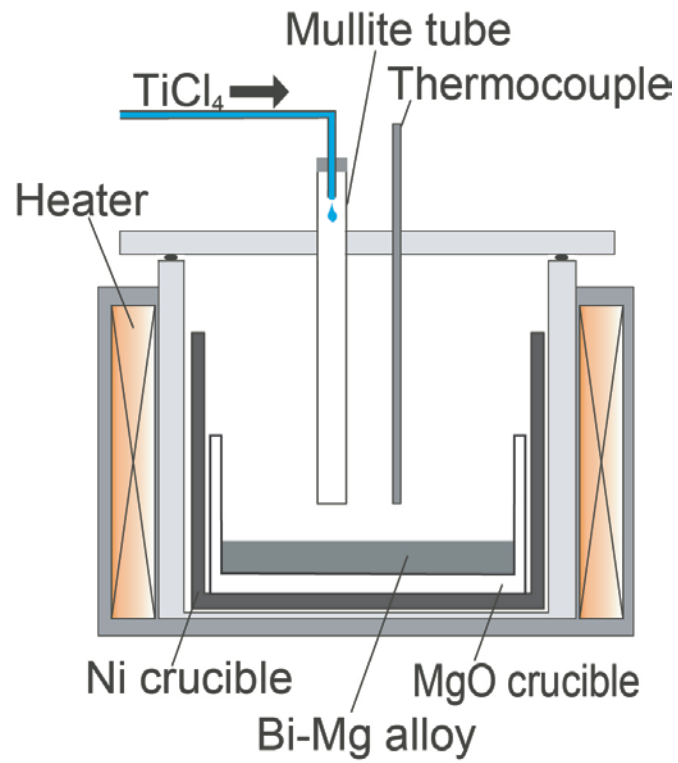


Figure 2 Experimental apparatus for magnesiothermic reduction of  $\text{TiCl}_4$  into liquid Bi.

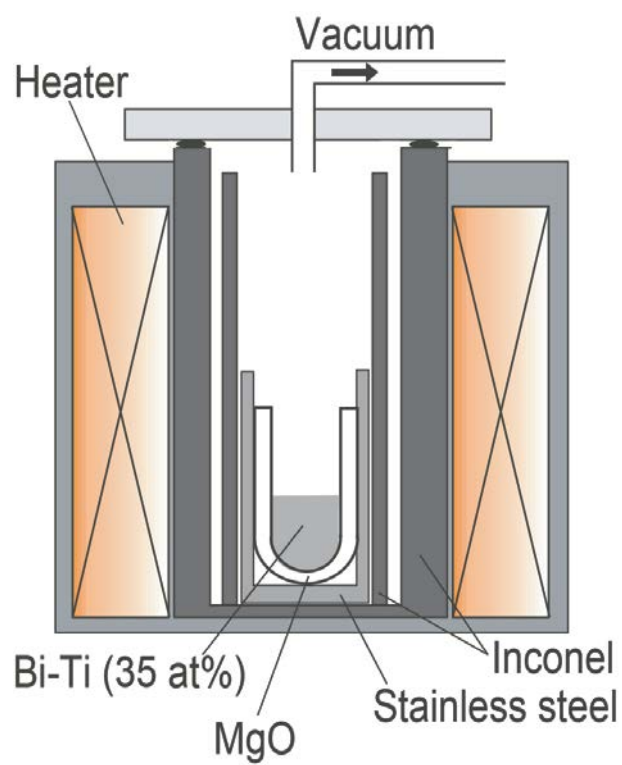


Figure 3 Experimental setup for vacuum distillation of the Bi–Ti alloy.

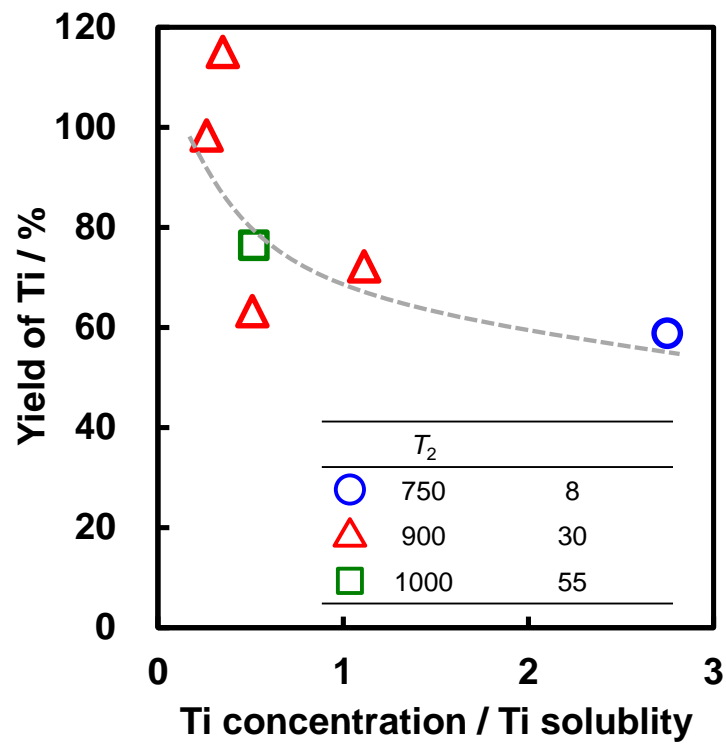


Figure 4 Ti yields plotted as a function of the ratio of the Ti concentration in the alloy to the Ti solubility in Bi. The inset denotes the holding temperature,  $T_2$ , and Ti solubility at each temperature.

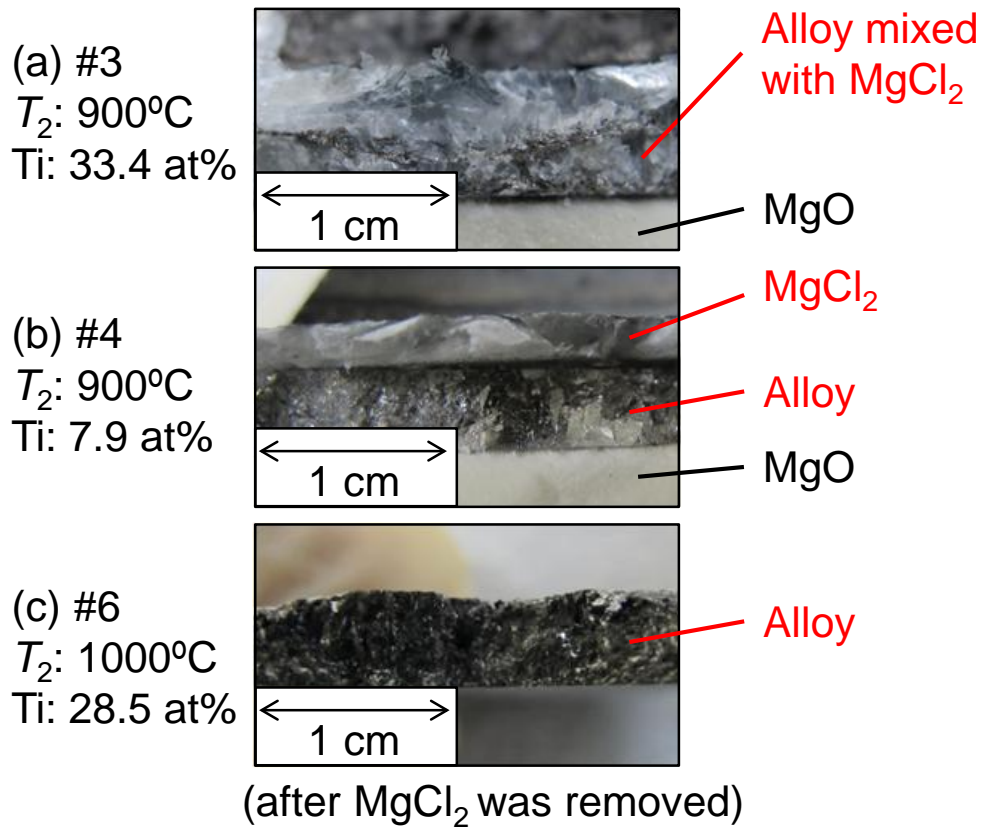


Figure 5 Optical cross-sectional images of the Bi-Ti alloys obtained after Exp. #3 (a), 4 (b), and 6 (c).  $\text{MgO}$  and  $\text{MgCl}_2$  were removed for Exp. #6.

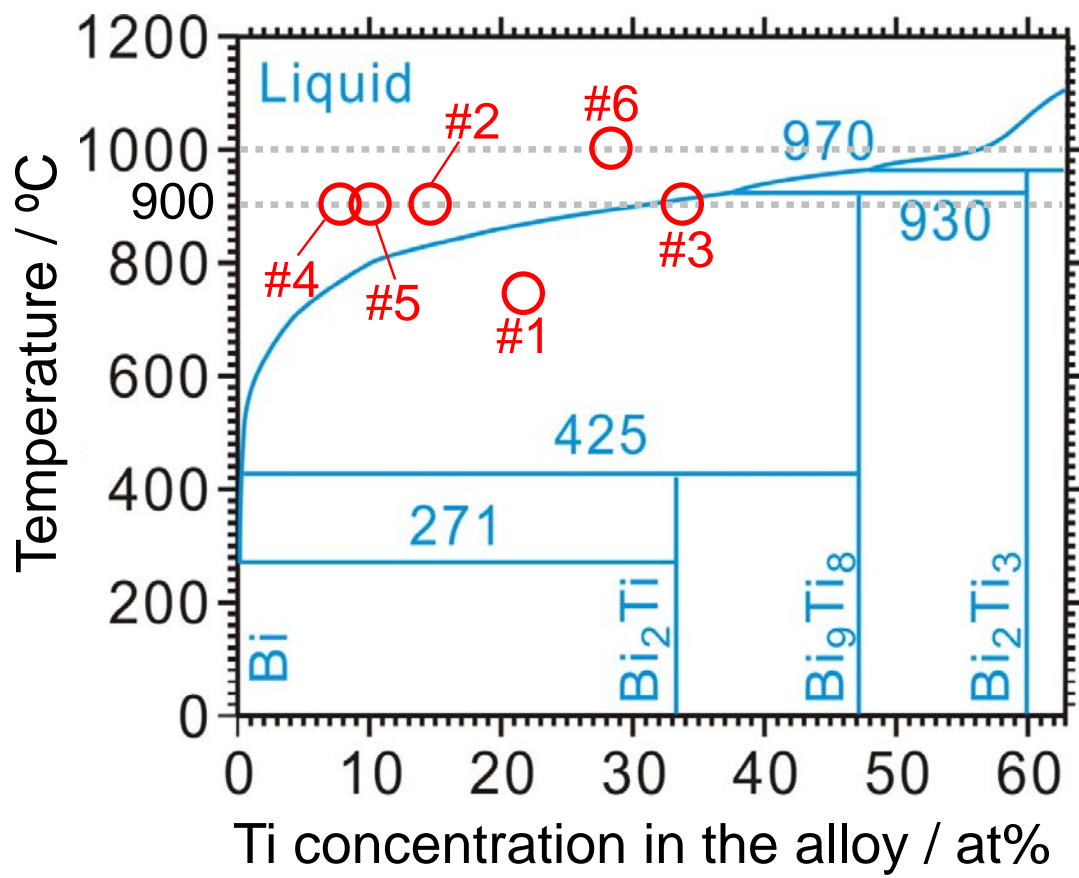


Figure 6 A part of the phase diagram of the Bi-Ti system with the obtained concentration of Ti in our experiments.

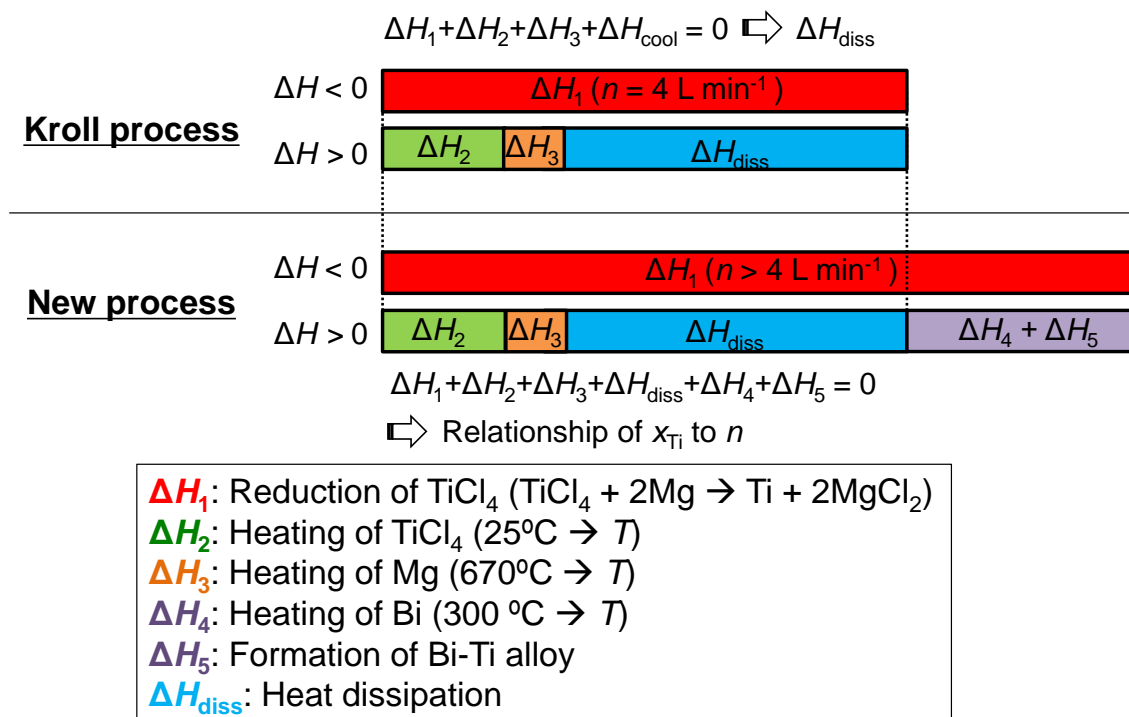


Figure 7 Consideration of heat balance in magnesiothermic reduction of  $\text{TiCl}_4$  into liquid Bi.

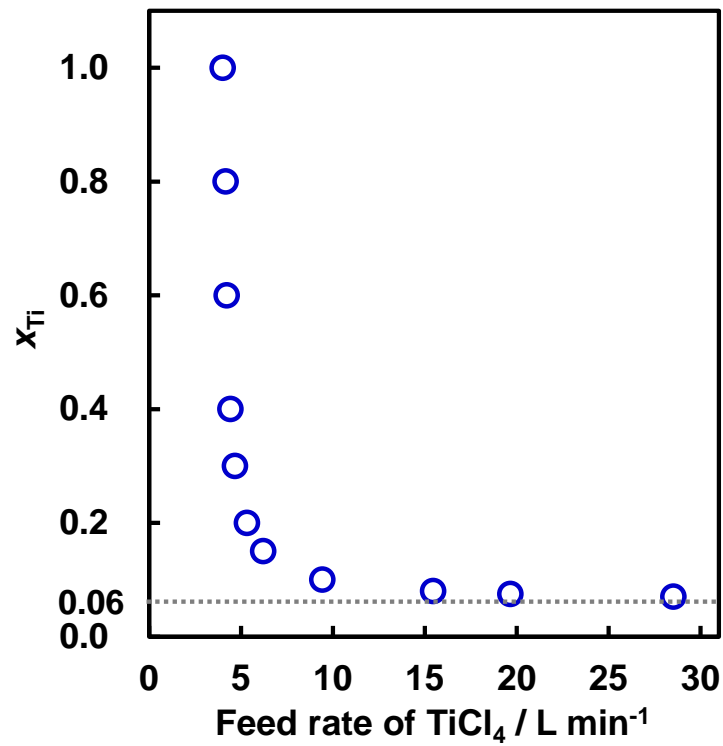


Figure 8 Relationship between  $x_{\text{Ti}}$  and the feed rate of  $\text{TiCl}_4$  determined by the heat balance consideration in the reduction step. Suppose the feed rate of  $\text{TiCl}_4$  in the Kroll process is  $4 \text{ L min}^{-1}$  [8,9].